(54) PROCESS FOR PRODUCING A COPOLYMER OF TETRAFLUOROETHYLENE AND PROPYLENE

(71) We, ASAHI GLASS COMPANY LIMITED, a Japanese Company of No. 1-2 2-chome, Marunouchi, Chiyoda-ku, Tokyo, Japan, do hereby the invention, for which we 5 pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement: —

The present invention relates to a process 10 for producing a copolymer of tetrafluoroethylene and propylene. It has been known to produce a copolymer of tetrafluoroethylene and propylene by suspension polymerisation of tetrafluoroethylene and propylene in the 15 presence of an organic peroxide catalyst (British Patent No. 594249) or by emulsion polymerisation of tetrafluoroethylene and propylene in the presence of a water soluble catalyst (U.S. Patent No. 3467635).

20 These processes however, have the disadvantages of requiring a high pressure (about 150 kg/cm²) so as to require in turn comprehensive and heavy apparatus. Moreover, the polymerisation reaction rate is too slow and the purifica- 25 tion of the copolymer is difficult. It has also been known to produce a copolymer of tetrafluoro ethylene and propylene by irradiation of ionizing radiation (Kogyo Kagaku Zasshi 68 (10) 1926-9). This process has the advantage 30 of yielding a pure product, but has the disadvantages of slow polymerisation reaction rate such as 0.1%/hour and of a low degree of polymerisation and further of difficulty of removal of heat of reaction, so that this pro- 35 cess is hard to carry on an industrial scale.

According to the invention there is provided a process for producing a copolymer of tetrafluoroethylene and propylene which comprises 40 mixing the monomers with a liquid medium which is capable of dissolving or swelling the copolymer and subjecting the mixture to free-radical producing radiation.

Preferably the radiation is an ionising radia- 45 tion, e.g. from a radioactive source such as Cobalt 60.

The preferred process to be described yields a copolymer of tetrafluoroethylene and propylene at a high polymerisation reaction rate, with a narrow distribution of molecular weight 50 and at relatively low pressures and temperatures.

The molar ratio of tetrafluoroethylene to propylene can be selected within a broad range such as tetrafluoroethylene/propylene 55 (molar ratio) 99/1 to 1/99, preferably 99/1 to 30/70, especially 95/5 to 50/50. The degree of polymerisation and composition of said copolymer depend upon the molar ratio of tetrafluoroethylene charged. With high con- 60 centrations of tetrafluoroethylene the molecular weight of said copolymer is sufficiently high and the copolymerisation reaction rate is suitable and moreover, solvent resistant of the copolymer is high. 65

The following matters should be considered in selecting the medium.

(a) The medium should preferably have the property of accelerating the polymerisation reaction rate, in the initiation and/or propaga- 70 tion stage of reaction.

For example, diethylether or tetrahydrofuran gives copolymerisation reaction rates which are the same as that in the known radiation processes (where no medium is 75 employed), accordingly they are not recommended for the present invention.

(b) The medium should preferably not prevent or slow down the production rate of radicals of tetrafluoroethylene or propylene. 80

The copolymerisation proceeds via a free radical process by irradiation of ionising radioactive rays.

For example, benzene or toluene retards the formation of free radicals and accordingly less 85 copolymer results.

(c) The medium should preferably not be liable to chain transfer with the reactants under the irradiation.

The molecular weight of copolymer is 90 decreased by chain-transfer, and a liquid copolymer is produced.

Chloroform, carbon tetrachloride and dichloroethane have such transfer action and accordingly they are not to be preferred as the medium.

5   (d) The medium should be liquid under the reaction conditions. It is necessary to react in the liquid phase.

(e) The medium should preferably dissolve at least one of the monomers tetrafluoroethylene 10 or propylene to make a reasonably and preferably completely homogeneous copolymerisation reaction system. For example, t-Butanol dissolves only propylene, but fluorohydrocarbons and fluorochlorohydrocarbons dissolve 15 both tetrafluoroethylene and propylene.

(f) The medium should be a swelling agent or solvent for the resulting copolymer, but should be non-polymerisable. Fluorohydrocarbons or fluorochlorohydrocarbons are good 20 solvents and t-Butanol has such properties even though weakly.

(g) The medium may e.g. have a boiling point of $-10°C$ to $+100°C$.

(h) Fluorohydrocarbons or fluorochloro- 25 hydrocarbons having 1 to 4 carbon atoms are the most preferable medium for the present invention.

With the use of this medium, high molecular weight copolymers having sharp distribution 30 of molecular weight can effectively be produced at high copolymerisation reaction rates, a homogeneous copolymerisation reaction system results and accordingly good reproducibility is obtained.

35   The preferred medium includes chlorofluorohydrocarbons such as monofluorotrichloromethane, trifluorotrichloroethane, tetrafluorodichloroethane; fluorohydrocarbons such as perfluorocyclobutane, n-Butanol and t-Butanol 40 can also be employed as the medium, though the distribution of molecular weight of resulting copolymer is little broader in comparison with that of the copolymer produced in the presence of chlorofluorohydrocarbon or fluoro-45 hydrocarbon.

n-Butanol and t-Butanol can dissolve said monomers but slightly swell said copolymer.

The molar ratio of monomers of tetrafluoroethylene and propylene to said medium 50 depends upon the type of medium, reaction temperature, molar ratio of tetrafluoroethylene to propylene and type of apparatus, and is usually 1/10 to 10/1 preferably 1/5 to 10/1 and especially 1/2 to 6/1. The molar ratio of 55 said monomers to said medium affects the copolymerisation reaction rate, molecular weight and distribution of molecular weight, but it does not affect the ratio of C_2F_4/C_3H_6 in the resulting copolymer.

60   Although tetrahydrofuran is a solvent of said copolymer, it hinders copolymerisation. Benzene is a deactivator of said copolymerisation.

As ionizing radiation, γ-rays, X-rays, α-rays, 65 β-rays and electron rays or some or all of them may be used. The dose rate of said ionizing radiation may be in the range of 100 to 1,000,000 roentgen/hour, preferably 1000 to 100,000 roentgen/hour.

In general, in the case of a high dose rate, 70 the copolymerisation reaction rate is high, but the molecular weight of copolymer is low.

The reaction of copolymerisation in this invention can be carried out within a range of temperature of $-40°$ to $150°C$ preferably 75 $-20°$ to $+100°C$.

The reaction pressure can be lower than those of known processes and can be less than 100 kg/cm², preferably 1 to 50 kg/cm², especially 5 to 30 kg/cm².   80

It is an advantage of the present invention that distribution of molecular weight can be minimised and the following conditions of reaction are preferred.

(a) Molar ratio of C_2F_4/C_3H_6 85
   The distribution of molecular weight is broader, when tetrafluoroethylene is too rich.

(b) Ratio M/S (monomers/medium)
   The distribution of molecular weight is 90 broader when the ratio M/S is higher than 50/50.

(c) Dose rate
   The distribution of molecular weight is narrow when the dose rate of irradiation 95 is 100 to 1,000,000 roentgen/hour.

(d) Reaction period
   The distribution of molecular weight is broader when the reaction period is too long.   100

In the preferred process of this invention, tetrafluoroethylene and propylene are respectively charged at a predetermined ratio, in a reactor through valves of respective pressured containers, and said medium is further charged 105 in the reactor and then the contents of the reactor are repeatedly solidified and the air removed. In commercial scale production the air in the autoclave is substituted with nitrogen gas.   110

The contents of the reactor are irradiated at a predetermined dose rate, for a suitable time. The resulting copolymer of tetrafluoroethylene and propylene is obtained by discharging unreacted monomer and said medium as gas, and 115 drying the product in a vacuum.

If desired, the resulting product can be purified by dissolving it in a solvent such as tetrahydrofuran and re-precipitated by adding methanol.   120

The reaction is usualy made under relatively low pressure such as 10 atms., though the mixture of said raw materials and said medium is in liquid phase.

The polymerisation reaction rate is quite 125 high and the inherent viscosity of the resulting copolymer is high, and the reaction temperature is quite easily controlled, because of dispersion of heat of reaction through said medium. This reaction also can be carried on 130

in a wide range of $-40°$ to 150°C, though it is usual to react at about 0°C. Moreover, there is no difficulty of purification of resulting product, and the properties of the copolymer can be changed by selecting the molar ratio of tetrafluoroethylene to propylene, and the distribution of molecular weight of the copolymer can be controlled by selecting the distribution of dose rate of radioactive radiation.

A distribution of molecular weight of copolymer is shown as $\overline{Mw}/\overline{Mn}$, wherein $\overline{Mn}$ is the number average molecular weight and $\overline{Mw}$ is the weight average molecular weight which are measured by Gel Permiation Chromatography (e.g. with apparatus manufactured by Waters Associates Co.). The degree of polymerisation can be shown by the inherent viscosity in tetrahydrofuran. The molecular weight of the copolymer is preferably more than 20,000 which approximately corresponds to an inherent viscosity of more than $[\eta]$ of 0.2.

The following examples are intended merely to describe specific embodiments of the present invention, in comparison with those of known processes.

Example 1

An autoclave made of stainless steel and having 100 cc volume was charged with 21.4 g tetrafluoroethylene, 5.1 g propylene and 63.7 g trifluorotrichloroethane, and air was removed by repeating melting — solidifying — evacuating and the autoclave was cooled in ice water at 0°C.

The contents were subjected to irradiation by γ-rays given by Cobalt 60 at a dose rate of 3.0 × 10⁵ roentgen/hour for 5 hours, and unreacted monomer and said medium were discharged and 10.3 g copolymer of tetrafluoroethylene and propylene was obtained.

The polymerisation reaction rate was 7.8% /hour, and the content of tetrafluoroethylene in said copolymer was 49 mole %, and the inherent viscosity of said copolymer in tetrahydrofuran solution (100 cc/g) at 30°C was 0.19.

(Reference)

The process according to Example 1 was repeated employing 74.4 g tetrafluoroethylene, and 15.6 g propylene without adding any medium, and irradiating for 10 hours. As the result 19.1 g copolymer of tetrafluoroethylene and propylene having a tetrafluoroethylene component of 49 mol % was obtained. However, the polymerisation reaction rate was 1.9%/hour, and the inherent viscosity of said copolymer in tetrahydrofuran (100 cc/g) at 30°C was 0.12.

Examples 2 to 8

In an autoclave made of stainless steel having 100 cc volume, tetrafluoroethylene, propylene and medium were charged and air was removed by repeted melting — solidifying — evacuating and the autoclave was maintained at the specified temperature.

The contents were subjected to radiation from γ-rays given by Cobalt 60 and then unreacted monomer and said medium were discharged to obtain each specified copolymer of tetrafluoroethylene and propylene. The yield, content of tetrafluoroethylene, polymerisation reaction rate and inherent viscosity of said copolymer in tetrahydrofuran and appearance are stated in the following Table 1.

TABLE 1

Example No.	Monomers contents			Medium		Radiation			Yield (g)	Copolymer			Mechanical property
	TFE* (g)	P* (g)	TFE*/P* (Molar ratio)	Type	Amount (g)	Dose rate (γ/hr)	Temp. (°C)	Time (hr)		TFE Content (%)	Polymerization reaction rate (%/hr)	Inherent viscosity	
2	27.8	5.6	2/1	MFTCM	51.5	3.0×10^5	0	5	12.5	49	7.5	0.18	
3	21.2	4.6	2/1	PFCB	64.0	,,	0	5	4.8	50	3.7	0.22	rubber like elasticity
4	21.4	5.1	2/1	TFTCE	63.7	,,	—40	5	2.6	48	2.0	0.09	
5	,,	,,	,,	,,	63.7	,,	100	1	12.8	51	50.0	0.23	rubber like elasticity
6	32.3	1.4	9/1	,,	66.3	,,	0	0.75	5.1	54	20.0	0.5	rubber like elasticity
7	21.4	5.1	2/1	,,	63.7	4.4×10^3	0	10	1.3	49	0.5	0.3	rubber like elasticity
8	21.4	5.1	2/1	t-Butyl alcohol	48.0	,,	0	10	21.2	50	8.1	90.3	rubber elasticity

Note: * TFE: tetrafluoroethylene

     * P: propylene

     MFTCM: monofluorotrichloromethane

     PFCB: perfluorocyclobutane

     TFTCE: trifluorotrichloroethane

In order to show the advantages of this invention, in comparison with no addition of said medium, the results of experiments on production of copolymers of tetrafluoroethylene and propylene with and without adding said medium are shown in Tables 2 and 3.

Experiment 1

In an ampule of 25 cc, tetrafluoroethylene and propylene were copolymerised under irradiation of γ-rays. The conditions of reaction temperature, molar ratio of C_2F_4/C_3H_6,

molar ratio of monomer to medium, dose rate of γ-rays and irradiation time are stated in Table 2.

The results as yield, (weight %), number average molecular weight (hereinafter referred to as $\overline{Mn}$), weight average molecular weight (hereinafter referred to as $\overline{Mw}$), distribution of molecular weight (hereinafter referred to as $\overline{Mw}/\overline{Mn}$) and inherent viscosity of copolymer in tetrahydrofuran ([η]) are also stated in the Table 2.

TABLE 2

Medium	Temperature (°C)	C_2F_4/C_3H_6 molar ratio	Monomer/ medium	Dose rate (r/hr)	Irradiation time (hrs)	Yield (wt %)	$\overline{Mn}$ (×10000)	$\overline{Mw}$ (×10000)	$\overline{Mw}/\overline{Mn}$	[η]
TFTCE*	—	66/34	1	5.0×10^4	4.0	13.4	2.5	4.3	1.73	0.26
,,	,,	,,	,,	,,	9.0	27.6	2.4	4.2	1.73	0.25
,,	,,	,,	,,	,,	13.5	41.7	2.3	4.0	1.73	0.26
,,	—	90/10	,,	,,	2.5	11.9	3.2	5.9	1.83	0.31
,,	,,	66/34	,,	2.2×10^4	6.0	7.3	2.7	4.8	1.74	0.35
,,	75	,,	,,	5.0×10^4	5.0	42.7	2.4	4.1	1.72	0.25
,,	—	,,	4	,,	7.5	17.0	3.0	5.5	1.83	0.27
t-Butanol	,,	,,	1	3.0×10^5	5.0	40.7	2.6	5.8	2.26	0.35
none medium	−23	66/34	,,	,,	10.0	14.5	2.2	6.5	2.92	0.30
none medium	,,	90/10	,,	,,	5.5	10.5	2.8	8.9	3.17	0.54
,,	,,	,,	,,	6.9×10^4	6.0	5.3	3.6	12.9	3.55	0.71

Note: * TFTCE: trifluorotrichloroethane

Mw/Mn shows the distribution of molecular weight. In the case of random distribution, Mw/Mn is 2.0. As shown in Table 2, in each case using trifluorotrichloroethane, Mw/Mn is less than 2.0 which shows a narrow distribution of molecular weight of copolymer.

In the case of t-butanol, Mw/Mn is 2.26 which shows a rather broad distribution of molecular weight, although the molecular weight itself is quite high.

Where no medium is used, Mw/Mn is quite high which shows a broad distribution of molecular weight. If the resulting copolymer is not dissolved in the monomer, the copolymerisation is made in a two phases system in the case of mass polymerisation.

On the other hand, if the resulting copolymer is dissolved in the medium, the copolymerisation is made in a one phase system.

Experiment 2

In an autoclave having a volume of 5l, tetrafluoroethylene and propylene were copolymerised under irradiation of γ-rays.

The conditions of reaction and the results in each experiment are stated in Table 3.

TABLE 3

Medium	Temperature (°C)	C_2F_4/C_3H_6 molar ratio	Monomer/ medium	Dose rate (r/hr)	Irradiation time (hrs)	Yield (wt %)	$\bar{M}n$ (×10000)	$\bar{M}w$ (×10000)	$\bar{M}w/\bar{M}n$	[η]
*TFTCE	0	75/25	4	5×10^4	20	25.8	3.4	7.3	2.17	0.42
"	"	"	"	"	"	34.4	3.4	7.4	2.21	0.47
"	"	"	"	"	"	30.6	3.5	8.0	2.28	0.37
"	"	"	"	"	8	11.2	2.7	4.7	1.76	0.33
"	0	"	"	"	20	36.8	3.0	6.0	2.04	0.38
t-Butanol	0	75/25	4	5×10^4	17	17.7	2.9	7.2	2.48	0.40
None medium	0	90/10	—	4.5×10^4	18	7.9	0.73	3.5	4.80	0.69
"	28	66/34	—	4×10^4	17	34.1	2.9	9.0	3.16	0.44

Note: * TFTCE: trifluorotrichloroethane

Experiment 3

In an autoclave made of stainless steel or an ampule, tetrafluoroethylene and propylene were copolymerised under irradiation of γ-rays, in order to clarify the effect of a molar ratio of two monomers and the ratio of monomers to medium. Each condition of copolymerisation is stated in the Table 4.

In each experiment, trifluorotrichloroethane was used as the medium and the reaction temperature was 0°C and the dose rate of γ-rays was 5×10^4 roentgen/hour.

TABLE 4

No.	C_2F_4/C_3H_6	M/S	Irrd. time	Yield (wt %)	$\overline{Mn} \times 10^{-4}$	$\overline{Mn} \times 10^{-4}$	$\overline{Mw}/\overline{Mn}$	$[\eta]$	C_2F_4/C_3H_6
1	66/34	4	8	17	2.2	4.4	2.00	0.24	50/50
2	75/25	4	20	20	3.5	8.0	2.28	0.37	51/49
3	90/10	4	5	11	2.5	5.8	2.3	0.37 $\overline{Mn}=4.6$ ($\times10000$)	54/46
4	90/10	4	10	23	3.2	8.3	2.6	0.44 $\overline{Mn}=5.5$ ($\times10000$)	55/45
5	66/34	1/4	13	36	1.8	3.2	1.8	0.20	51/49
6	66/34	1/1	3	10	2.5	4.3	1.7	0.26	50/50

In the Experiments of Nos. 1, 2, 5 and 6, 20 cc ampoules were used as reactor. On the other hand, in Experiments of Nos. 3 and 4, a 5l autoclave was used as reactor.

In Experiment No. 4, propylene monomer was added to tetrafluoroethylene for 5 hours to reach the predetermined ratio ($C_2F_4/C_3H_6 = 90/10$) and then the reaction was continued for a further 5 hours.

The value of $\overline{Mn}$ measured by the Gel Permiation Chromatography was less than actual value of the weight average molecular weight.

Where no medium was used the ratio $\overline{Mw}/\overline{Mn}$ was quite high, which shows a broad distribution of molecular weight.

On the other hand in each case where the trifluorotrichloroethane was added, the ratio $\overline{Mw}/\overline{Mn}$ was about 2.0 even though the molecular weight was quite high.

These results show a narrow distribution of molecular weight.

Where t-butanol was added, the ratio $\overline{Mw}/\overline{Mn}$ was 2.48 which is low by comparison with the case without medium.

WHAT WE CLAIM IS:—

1. A process for producing a copolymer of tetrafluoroethylene and propylene which comprises mixing the monomers with a liquid medium which is capable of dissolving or swelling the copolymer and subjecting the mixture to free-radical producing radiation.

2. A process as claimed in claim 1 wherein the radiation is an ionising radiation.

3. A process as claimed in claim 1 wherein a radioactive source is used to generate the radiation.

4. A process as claimed in claim 3 wherein the radioactive source is Cobalt 60.

5. A process as claimed in any preceding claim wherein the said medium is a solvent for at least one of the monomers.

6. A process as claimed in claim 5 wherein the said medium is a solvent for both monomers.

7. A process as claimed in any preceding claim wherein the solvent is selected for its property of accelerating the rate of reaction and not hindering the production of free radicals and which is not subject to chain transfer with one or both monomers.

8. A process as claimed in any preceding claim wherein the said medium is chlorofluorohydrocarbon or a fluorohydrocarbon.

9. A process as claimed in any of claims 1 to 6 wherein said medium is t-butyl alcohol.

10. A process as claimed in any preceding claim wherein the molar ratio of said monomers to said medium is from 1/10 to 10/1.

11. A process as claimed in claim 10 wherein said molar ratio is from 1/2 to 6/1.

12. A process as claimed in any preceding claim wherein the reaction pressure is from 1 to 50 kg/cm².

13. A process as claimed in any preceding claim wherein the molar ratio of tetrafluoroethylene to propylene is from 95/5 to 50/50.

14. A process as claimed in any preceding claim conducted at a temperature from – 20°C to +100°C.

15. A process as claimed in any preceding claim wherein the medium is a compound as hereinbefore set forth.

16. A process as claimed in claim 1 substantially as described herein with reference to the Examples or Experiments.

17. A copolymer of tetrafluoroethylene and propylene produced by the process claimed in any preceding claim.

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